THE REACTION OF STABLE SULFONIUM YLIDES OF DIMEDONE WITH TRIPHENYLPHOSPHINE

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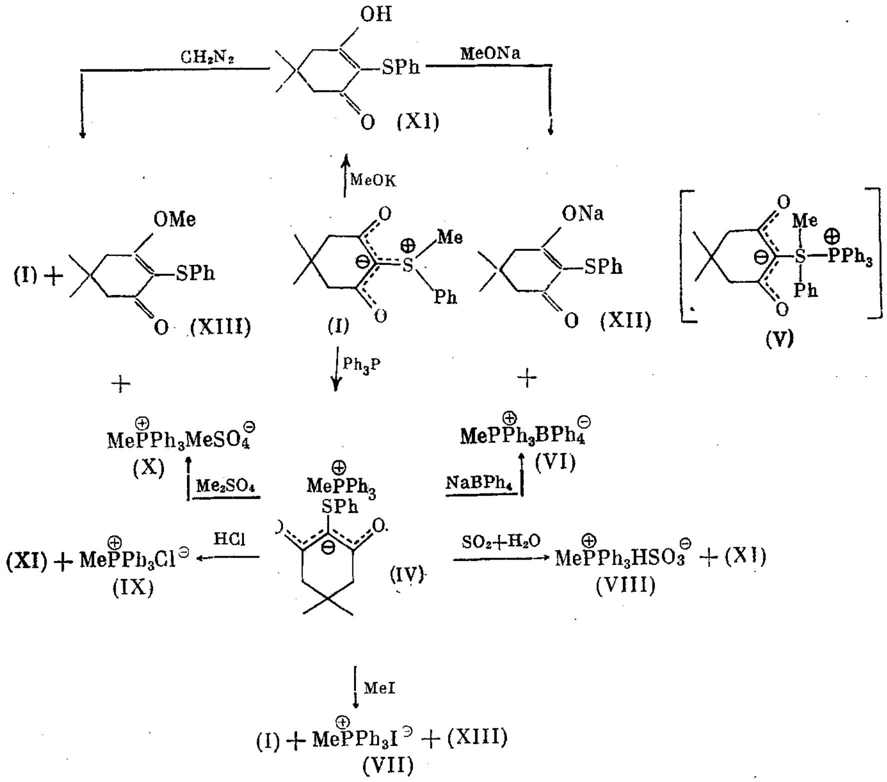
Triphenylphosphine (TPP) is capable of desulfurizing [1] or transylidating [2] stable sulfonium ylides. We have investigated the reactions of TPP with 2-[methylphenyl- (I), 2-dimethyl- (II), 2-dibenzyl- (III) sulfuranylidene]-5,5-dimethylcyclohexane-1,3-dione. We found that TPP demethylates (I) to form methylphosphonium-2-(phenylthio)-5,5-dimethylcyclohexane-1,3-dione (IV).

Demethylation occurs either by attack by TPP on the electrophilic carbon of the S-methyl group, as has been suggested for the reactions of sulfonium ylides with methoxide or acetyl anion [3, 4] or the electrophilic sulfur is attacked and the intermediate sulfuranylphosphonium betaine (V) decomposes to salt (IV), although in the latter case transylidation seems more probable



We established the structure of salt (IV) from its physicochemical properties. We found that the electrical conductivity of (IV) in DMF (λ_i = 26.0) is comparable to that of methyltriphenylphosphonium tetraphenylborate (VI) (λ_i = 30.5).

The UV spectrum of (IV) is MeOH shows the phenyl K band in the 220-230 nm region and complex absorption in the 258-286 nm region, consisting of the phenyl B band and the partly overlapping carbanion absorption band (inflection at 282-286 nm). The B band has slightly smoothed fine structure. Attempted induction of a bathochromic shift of the carbanion absorption band (the UV spectrum in DMSO, which is a strongly coordinating solvent [5]) was

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unsuccessful — we detected no changes in the spectrum. Obviously the bulky ions of (IV) are only weakly solvated even in DMSO and exist as contact ion pairs [5]. Although in position and character of the bands the UV spectrum of (IV) resembles that of methyltriphenylphosphonium iodide (VII) [6], the intensity of the long-wavelength band in (IV) is much greater, plainly as a result of the contribution of the absorption of the carbanion system.

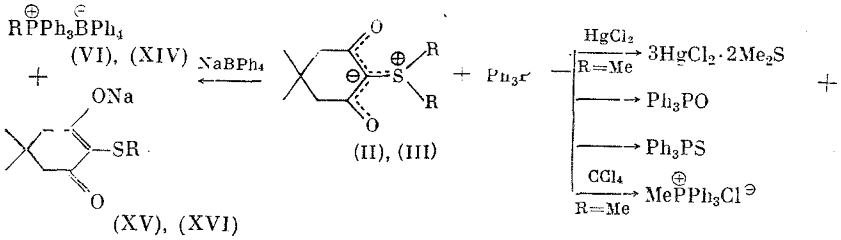
The IR spectrum of (IV) shows $\nu_{C\cdots C\cdots O}$ = 1520 cm^{-1}, which implies considerable delocalization of electron density in the carbanion system. The IR spectrum of (IV) also shows bands characteristic for the methyltriphenylphosphonium cation [7, 8]: the multiplet of bands at 700-800 cm^{-1} represents the phenyl C-H deformation modes; the band at 900-920 cm^{-1} represents the PCH_3 deformation mode; and the band at 1120 cm^{-1} is characteristic for TPP and its derivatives. The PMR spectrum of (IV) shows the PCH_3 protons as a doublet at δ 2.95 ppm ($^2J_{PH}$ = 14 Hz), consistent with [9]. The ^{31}P chemical shift is 18 ppm, which is normal for compounds of this type [10].

To confirm the structure of salt (IV) we examined its chemical properties. We found that the anion-exchange reactions of (IV) with $NaBPh_4$, MeI, moist SO_2 (gas), dry HCl (gas), and Me_2SO_4 form methyltriphenylphosphonium salts (VI)-(X). Salts (VI), (VII), and (IX) have been described [10]. We established the structures of salts (VIII) and (X) from their physicochemical properties and elemental analyses.

In character, position, and intensity of the bands the UV spectrum of (X) resembles that of salt (VII) [6]. The IR spectra of (VIII) and (X) show all the bands characteristic for methyltriphenylphosphonium salts [7, 8]. The PCH_3 doublets in the PMR spectra of (VIII) and (X) lie at 3.03 ppm ($^2J_{PH}$ = 13 Hz) and 2.96 ppm ($^2J_{PH}$ = 13 Hz) respectively. We were unable to detect the $HSO_3^{\ominus}$ proton, probably because of the low solubility of (VIII) in organic solvents. The $MeSO_4^{\ominus}$ protons appear at 3.46 ppm. The PMR spectra of both salts also show the phenyl multiplets in the 7.5-8.0 ppm region.

We were unable to isolate the products of the interaction of the carbanion system of salt (IV) with these reagents in the pure form. However an IR and PMR examination of the residue from the reaction mixtures after removal of the phosphonium salts suggests the following conclusions. Reaction of $NaBPh_4$ with (IV) converts the carbanion system to the Na salt of 2-(phenylthio)-5,5-dimethylcyclohexane-1,3-dione (XII); reaction with HCl or moist SO_2 forms 2-(phenylthio)-5,5-dimethylcyclohexane-1,3-dione (XI); reaction with MeI or Me_2SO_4 gives a mixture of sulfonium ylide (I) and 2-(phenylthio)-3-methoxy-5,5-dimethylcyclohexen-2-one (XIII). Treatment of a reaction mixture containing (XII) or (XIII) with dilute HCl readily forms (XI). To confirm these conclusions we synthesized compounds (XI)-(XIII) by independent routes. Compound (XI) is easily prepared by demethylation of (I) with methoxide anion [3]; reaction of (XI) with MeONa in MeOH forms (XII), while reaction of (XI) with CH_2N_2 gives a mixture of (I) and (XIII), in agreement with our earlier results [11]. Comparison of the IR and PMR spectra of the products derived from the carbanion system of salt (IV) with those of authentic samples of (XI)-(XIII) confirms our conclusions regarding their structures.

Study of the reactions of ylides (II) and (III) with TPP revealed that both desulfurization [1] and deoxygenation of the ylide take place; $Ph_3P=O$ is the major product, probably resulting from deoxygenation not only of the ylide but also of its initial reaction products. The reaction of (II) with TPP also gives Me_2S (isolated as its complex with $HgCl_2$ [12]) and salt (IX) [10]. The latter is probably formed by demethylation of (II) and reaction of the intermediate phosphonium salt with the CCl_4 used in the treatment of the reaction mixture. The diversity of the transformations of the carbanion system of ylides (II) and (III) precluded identification of intermediates that are capable of further reaction under the experimental conditions



(XV), (XVI)

R = CH_2Ph (III), (XIV), (XVI); Me (II), (VI), (XV)

+ Unidentified ring transformation products

We were unable to isolate salts of type (IV) from the reactions of (II) and (III) with TPP, probably because of their instability at high temperatures (140-170°C). Proof of the possibility of dealkylation of (II) and (III) by TPP is provided by the products of these reactions in the presence of $NaBPh_4$; we isolated salt (VI) and benzyltriphenylphosphonium tetraphenylborate (XIV). The unstable salts of type (IV) formed in these reactions may be stabilized by anion-exchange reactions with $NaBPh_4$. We identified the Na salts of (XV) and (XVI) formed in this reaction from their IR spectra: $\nu_{C\cdots C\cdots O}$ = 1500 cm^{-1} (vs, broad) [13]. The IR spectra of (XV) and (XVI) closely resemble that of salt (XII), which we describe below.

EXPERIMENTAL

Spectra were recorded with: a KGU-4 NMR spectrometer (10.2 MHz), external standard 85% H_3PO_4 (^{31}P NMR); a Varian T60 spectrometer (60 MHz), in CH_2Cl_2 or tetrachloroethane [salt (VIII)] relative to tetramethylsilane as internal standard (PMR); a UR-10 spectrometer, as mulls in Vaseline oil or films (IR); a Specord UV-VIS spectrophotometer (UV). Electrical conductivities were measured in DMF solution at 23°C at 1.3×10^{-2} –1.5×10^{-2} mole/liter. Optimum reaction conditions were derived from DTA results recorded with an NTR-70 instrument.

Preparation of Sulfonium Ylides (I)-(III). Ylides (I)-(III) were synthesized by condensation of dimedone with the appropriate sulfoxides in Ac_2O [for (I) and (II) see [14]]. The yield of (III) was 5%, mp 197-199°C (from benzene–petroleum ether). Found, %: C 75.26; H 7.01%. $C_{22}H_{24}O_2S$. Calculated, %: C 75.00; H 6.81%.

Reaction of Ylide (I) with TPP. Compound (I) (1.3 g) and TPP (3.9 g) were refluxed in toluene (30 ml) for 1 h. The solvent was removed under vacuum; the residue was treated with hot benzene to remove unreacted TPP. Recrystallization of the residue from CH_2Cl_2– ether gave (IV), yield 1.37 g (55%), mp 205-207°C. Found, %: C 75.87; H 6.33; S 6.26; P 6.07%. $C_{33}H_{33}O_2SP$. Calculated, %: C 75.57; H 6.29; S 6.10; P 5.91%.

Reaction of Methyltriphenylphosphonium-2-(phenylthio)-5,5-dimethylcyclohexane-1,3-dione (IV) with $NaBPh_4$, MeI, Moist SO_2 (H_2SO_3), Dry HCl, and Me_2SO_4. A solution of salt (IV) (4 mmole) in CH_2Cl_2 (10 ml) was treated by bubbling through for 1 h dry HCl (gas) or moist SO_2 (gas), or by addition of MeI, Me_2SO_4 (in 10 ml CH_2Cl_2), or $NaBPh_4$ (in 10 ml THF) (4 mmole of reagent in each case); the mixture was left at ~20°C for 3-6 days. After removal of the solvent the residue was treated with CH_2Cl_2 (15-20 ml). Phosphonium salts (VI)-(X) were precipitated with ether. The residue containing (I), (XI), and (XIII) was an uncrystallizable oily liquid, which was examined by IR and PMR spectroscopy without further purification. The residue containing (XII) was a high-melting powder, insoluble in the majority of organic solvents and not amenable to purification.

Methyltriphenylphosphonium tetraphenylborate (VI), yield 60%, mp 197-199°C [10]. Methyltriphenylphosphonium iodide (VII), yield 60%, mp 187°C [10]. Methyltriphenylphosphonium hydrogen sulfite (VIII); yield 32%, mp 202-203°C. Found, %: C 63.07; H 5.34; S 9.04; P 8.59%. $C_{19}H_{19}O_3SP$. Calculated, %: C 63.68; H 5.30; S 8.93; P 8.65%. Methyltriphenylphosphonium chloride (IX), yield 31%, mp 222-223°C [10]. Methyltriphenylphosphonium methyl sulfate (X), yield 46%, mp 149-152°C. Found, %: C 61.35; H 5.76; S 8.44; P 7.51%. $C_{20}H_{21}O_4SP$. Calculated, %: 61.85; H 5.41; S 8.24; P 7.98%.

Preparation of 2-(Phenylthio)-5,5-dimethylcyclohexane-1,3-dione (XI). Compound (XI) was prepared by treating (I) (2.62 g) with excess alcoholic KOH [3], yield 2.2 g (88%), mp 120-121°C (from benzene–petroleum ether). Found, %: C 68.05; H 6.50%. $C_{14}H_{16}O_2S$. Calculated, %: C 67.74; H 6.45%.

Preparation of the Sodium Salt of 2-(Phenylthio)-5,5-dimethylcyclohexane-1,3-dione (XII). An equimolar quantity of (XI) was dissolved in a solution of MeONa in MeOH. The MeOH was removed under vacuum and the residue was crystallized by adding ether. Compound (XII) was a white powder, identified from its IR spectrum: $\nu_{C\cdots C\cdots O}$ = 1500 cm^{-1} (vs, broad) [13].

Reaction of (XI) with CH_2N_2. A cooled solution of (XI) (1.4 g) in CH_2Cl_2 (10 ml) was added to an ethereal solution of CH_2N_2. After 1 h excess CH_2N_2 and ether were removed under vacuum. The residual oil (1.12 g) was chromatographed on SiO_2. Elution with benzene–acetone (2:1) gave (I) (0.44 g, 30%), mp 136-138°C and elution with benzene–ether (4:1) gave (XIII) (0.66 g, 45%), mp 84-85°C (from benzene–petroleum ether [11].

Reaction of Sulfonium Ylide (II) with TPP. Compound (II) (4 g) and TPP (5.2 g) in diglyme (50 ml) were refluxed until evolution of Me_2S ceased (2.5 h); Me_2S was trapped as its complex with $HgCl_2$ by passing the effluent gases into $HgCl_2$ solution (yield 0.6 g, 3.2%), mp 151°C [12]. At the end of the reaction the solvent was removed under vacuum; the residual oil was treated successively with hot petroleum ether, CCl_4, C_6H_6, and CH_2Cl_2. The petroleum ether gave $Ph_3P{=}O$ (2.55 g, 45%); the CCl_4 and C_6H_6 solutions on standing precipitated salt (IX) (0.34 g, 5%) as the monohydrate, mp 97-99°C [15], which easily lost water on warming to give (IX) with mp 222-223°C (from CH_2Cl_2–petroleum ether). The CCl_4-soluble oil yielded $Ph_3P{=}S$ (0.09 g, 2%), mp 160-162°C (from alcohol). Comparison with authentic samples identified $Ph_3P{=}O$ and $Ph_3P{=}S$.

Reaction of Sulfonium Ylide (III) with TPP. An equimolar mixture of (III) and TPP was heated in a sealed ampul to 170°C at 5-6 deg/min. The resulting oil was dissolved in CH_2Cl_2 and examined by IR spectroscopy and TLC on SiO_2. Comparison of the IR spectra of $Ph_3P{=}S$ and $Ph_3P{=}O$ with that of the reaction mixture and chromatography of the mixture with authentic $Ph_3P{=}O$ and $Ph_3P{=}S$ as standards revealed the presence of these compounds in the reaction mixture.

Reaction of Ylides (II) and (III) with TPP in the Presence of $NaBPh_4$. An equimolar mixture of (II) or (III), TPP, and $NaBPh_4$ was heated in a Stepanov sealed ampul to 170°C, whereupon the reaction mixture was cooled and treated with CH_2Cl_2. The white, CH_2Cl_2-insoluble powder was (XV) or (XVI), identified by its IR spectrum: $\nu_{C\cdots C\cdots O} = 1500\ cm^{-1}$ (vs, broad). Addition of ether to the extract precipitated crystals of (VI) or (XIV) in $\sim$50% yield. Compound (XIV): mp 223-224°C (from CH_2Cl_2–ether). Found, %: C 87.30; H 6.65; P 4.41%. $C_{49}H_{42}BP$. Calculated, %: C 87.50; H 6.25; P 4.61%.

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CONCLUSIONS

1. Triphenylphosphine demethylates 2-(methylphenylsulfuranylidene)-5,5-dimethylcyclohexane-1,3-dione to form methyltriphenylphosphonium 2-(phenylthio)-5,5-dimethylcyclohexane-1,3-dione (IV).
2. Compound (IV) readily undergoes anion-exchange reactions with $NaBPh_4$, MeI, moist SO_2 (gas), dry HCl, and Me_2SO_4.
3. Dimethyl- and dibenzylsulfonium ylides of dimedone are desulfurized and deoxygenated by triphenylphosphine.

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